Early draft

Uranium-Series Age Determination of Calcite Veins, VC-1 Drill Core, Valles Caldera, New Mexico

by

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Add: Fig 1. Location Map
Fig 2. Stratigraphy from ~~data~~ previous letter

ABSTRACT

Uranium-series analyses of 13 wide (>5 mm) calcite veins cutting the Madera Limestone in VC-1 drill core have been done in an attempt determine the age of the veins and to establish their relation to hydrothermal activity in the Valles hydrothermal system. The results indicate the following: the age of one of the veins is about 95 Ka; two of the veins probably formed about 200 Ka (with large uncertainty); five of the veins are near ($^{230}Th/^{234}U$) equilibrium, thus are probably older than about 300 Ka; and U concentrations in 5 other veins are too low for analysis with available sample amounts. Of the 5 veins near ($^{230}Th/^{234}U$) equilibrium, 4 are near ($^{234}U/^{238}U$) equilibrium, suggesting an age > about 1000 Ka, and 1 has ($^{234}U/^{238}U$) = 1.15 $\pm$ 0.09, suggesting an age between 300-1000 Ka. However, calculated initial ($^{234}U/^{238}U$) of the veins yielding relatively low ages are neither equal to each other nor identical to that of thermal water sampled in VC-1 (1.69 $\pm$ 0.22), thus age inferences based on ($^{234}U/^{238}U$) are uncertain. Three of the 4 veins yielding relatively low ages consist of coarse, sparry, vuggy calcite, indicating that this type of vein forms under conditions resembling those encountered presently in VC-1.

INTRODUCTION

Analysis of uranium series (U-series) disequilibrium in rocks, minerals, and waters has diverse applications in the earth and environmental sciences [Ivanovich and Harmon, 1982]. One of the principal applications is U-series disequilibrium geochronology, which is the only available means for determining the age of many relatively young geologic materials. Age determinations up to about 350 Ka by the $^{230}Th/^{234}U$ method are now done routinely; in some cases the amount of excess ^{234}U may allow determinations up to about 1000 Ka. However, applications of U-series geochronology in active hydrothermal systems have yet to be explored thoroughly; valuable information regarding the time scale of hydrothermal activity may be gained from such efforts, resulting in improved constraints for thermal and geochemical models of these systems. This paper presents the results of radioisotope dilution analyses of U and Th by alpha spectrometry in 13 calcite veins from the Madera Limestone in the VC-1 drill core (Valles Caldera, New Mexico). These data were obtained in an attempt to determine the age of the veins, and to thereby establish their relation to hydrothermal activity in the Valles hydrothermal system (Goff et al, this volume; Vuataz et al, this volume).

SAMPLES

Valles Caldera 1 (VC-1) was drilled to a total depth of 856 m near the southwestern rim of the caldera during the summer of 1984. The objectives and initial results of the drilling program were described by *Goff et al.*, [1986], and results of some subsequent VC-1 drill core studies are presented in this volume. Numerous calcite veins were found cutting the Madera Limestone in the VC-1 core [*Goff et al.*, 1986]. Representative samples of these veins were taken for this study from the heavily-veined intervals between 445-465 m and 720-805 m. Only "wide" veins of a size practical for radioisotope dilution analysis (>5 mm width) were sampled, resulting in a set of 13 samples. No other "wide" veins were observed in the entire Madera Limestone portion of the core on the date of sampling (April 16, 1986), thus all such veins are represented here except those that may have been completely removed ~~removed~~ previously by other investigators. Table 1 gives a brief description of each vein sampled, including piece number, depth in core, attitude, width, and appearance.

ANALYTICAL METHODS

Drill cores were sliced normal to calcite veins using a rock saw with distilled water as a lubricant. Saw marks and outer core surface were ground away with SiC grit paper. Calcite was separated from enclosing Madera Limestone with a fine chisel, crushed gently to <1 cm, cleaned ultrasonically in deionized distilled H_2O, and dried under a heat lamp. Calcite fragments were then inspected under a binocular microscope and those containing visible impurities were removed. Each sample was weighed, added to a Pyrex beaker previously cleaned in hot 16M HNO_3, and spiked with a solution of ^{229}Th and ^{236}U (activities calibrated to Th and U in NBS-610). Sample weights ranged from 1.1-18.9 g, depending on amount of sample available; 10 samples weighed less than 1.9 g. Each sample was dissolved in 8M HNO_3, and minor silicate residues of samples 344-5 and 346-10 were further treated with HF. After dissolution, samples were evaporated to dryness on a hot plate, then redissolved in 8M HNO_3 and loaded through filter paper onto a column of ~1.5 cc Bio-Rad AG1-X8 200-100 mesh anion exchange resin preconditioned with 8M HNO_3. Effluent solution containing U was collected in a clean beaker and evaporated to dryness. Th was retained on the column and eluted with 12M HCl that was then evaporated to dryness. The residue containing U was redissolved in 9M HCl and reloaded onto the same column after it had been rinsed with deionized distilled H_2O and preconditioned with 9M HCl. Effluent solution was discarded. U and Fe were eluted with 1M HCl that was then evaporated to dryness. Residue containing U and Fe was redissolved in a 20% 1M HNO_3 + 80% 2M AlNO3 solution (20/80 solution) and added to the same column after it had been rinsed with deionized distilled H_2O and preconditioned with 20/80 solution. Fe passed through the column and was discarded with 20/80 effluent. Al was eluted with 9M HCl and discarded. U was eluted finally with 1M HCl that was then evaporated to dryness.

Th and U were electrodeposited onto stainless steel planchets from a 1M NH_4Cl - 0.01 M oxalic acid solution, using a current of ~ 0.8 amp for ~1 hour. Alpha spectra were acquired for these planchets using low-background Si surface-barrier detectors. Corrections for reagent blanks and detector backgrounds in calcite analyses amounted to 0.9-4.6% of total peak areas for ^{230}Th, 1.5-5.3% for ^{234}U, <= 1.34% for ^{236}U (including subtraction of ^{235}U interference), and <= 0.61% for ^{229}Th. Total yields of the procedure ranged from about 30-70% for U and Th, with mean yields of 56% and 48%, respectively. Data reduction and ($^{230}Th/^{234}U$) age calculations were performed using a computer program adapted from UTAGE3 [Ivanovich and Harmon, 1982].

RESULTS AND DISCUSSION

Analytical results are shown in Table 2. Accurate age determinations for the veins analyzed are difficult or impossible for several reasons: (1) Concentrations of U are generally low. Five of the veins have less than 0.03 ppm U, the practical lower limit that is required for age determination, and none of the veins has more than 0.65 ppm U. These low concentrations coupled with the small amounts of material available for most of the vein analyses, have resulted in relatively large analytical uncertainties; (2) Concentrations of Th in most of the samples are high enough to cause uncertainties in age determination due to the initial activity of ^{230}Th; and (3) most of the samples having sufficient U for age determination have $(^{230}Th/^{234}U) = 1.00$ within analytical uncertainty, thus are beyond the age range of the $(^{230}Th/^{234}U)$ technique. Another important consideration is that the veins may have recrystallized subsequent to their initial deposition (with possible gain or loss of U), or may have experienced multiple growth episodes at different times, in which case the age inferred from the U-series data may be in error. Recent loss of U does not appear to be a problem, because none of the samples has $(^{230}Th/^{234}U)$ significantly greater than 1.00. However, recent gain of U could have affected samples having $(^{230}Th/^{234}U) < 1.00$, causing apparent ages less than the ages of initial deposition.

The assumptions can be made that the veins were deposited over a short time period relative to the half-life of ^{230}Th and have maintained a closed system with respect to U and Th since the time of their initial deposition. If so, then the following conclusions can be drawn regarding the time elapsed since their deposition: (1) The youngest vein analyzed is in sample 251-5, and was deposited at about 95 $\pm$ 14 Ka. Initial ($^{230}Th/^{232}Th$) as high as 2.00 would decrease the calculated age by only about 5 Ka; (2) Vein 225-12A has a calculated age near 220 Ka with a large uncertainty (Table 2). An initial ($^{230}Th/^{232}Th$) of 1.00 or 2.00 would decrease this by about 20 Ka or 90 Ka, respectively, therefore the calculated age listed in Table 2 should be considered an upper limit; (3) Vein 319-6 also has a calculated age near 220 Ka with a large uncertainty (Table 2). An initial ($^{230}Th/^{232}Th$) of 2.00 would decrease this by only about 30 Ka, which is within the quoted uncertainty of the calculated age; (4) Veins 225-9, 229-12B, 319-5, 344-5, and 346-10 have ($^{230}Th/^{234}U$) = 1.00 within analytical uncertainty (Table 2), indicating that their ages are probably beyond the resolution of the technique (i.e., >300 Ka). All but 225-9 also have ($^{234}U/^{238}U$) = 1.00 within analytical uncertainty; if initial ($^{234}U/^{238}U$) values were significantly greater than 1.00, then these veins are probably older than about 1000 Ka. Vein 225-9 has ($^{234}U/^{238}U$) = 1.15 $\pm$ 0.09, thus probably has an age between about 300 and 1000 Ka; and (5) Veins 228-11A, 326-5B, 327-16A, 343-17, and 347-6 have insufficient activities of U for age determination with the amounts of material available.

There is evidence that ~~groundwater~~ hydrothermal fluids at the VC-1 site ~~has~~ have had ($^{234}U/^{238}U$) >1.00 for the past few 10^5 years and ~~possibly~~ probably longer: (1) measured ($^{234}U/^{238}U$) in thermal water sampled during September, 1985 from VC-1 drill hole is 1.69 $\pm$ 0.22 (N. Sturchio et al., unpublished data, 1986); (2)

measured ($^{234}U/^{238}U$) for veins having ages ranging from 95 - >300 Ka are significantly greater than 1.00 (Table 2); and (3) initial ($^{234}U/^{238}U$) at Soda Dam appears to have been relatively high (~2.3) during periods of ~~travertine~~ deposition over the past ~10^6 years [Goff and Shevenell, in press]. Initial values of ($^{234}U/^{238}U$) have not been constant in VC-1, however, judging from those ~~calculated for the~~ samples having calculated ages <300 Ka, which range from 0.93 ± 0.14 to 4.16 ± 0.49 (Table 2). The uncertainty associated with the initial ($^{234}U/^{238}U$) renders difficult age determinations by the excess-(^{234}U) technique.

When the vein descriptions in Table 1 are compared to the analytical results in Table 2, a correlation can be seen. Among the veins having >0.03 ppm U, the relatively young veins are coarse, sparry, vuggy, and very wide, whereas the older veins are fine-grained and relatively thin, with one exception: vein 319-6 has a relatively young age but resembles the older veins in appearance. Vein 319-6 also bears a very strong resemblance to the nearby vein 319-5 that has ($^{230}Th/^{234}U$) near equilibrium; the analytical uncertainty is large enough to allow formation of both veins simultaneously at 240-325 Ka. The general similarity of most of the relatively young veins suggests that coarse, sparry, vuggy, and relatively wide calcite veins are deposited under conditions resembling those presently encountered in VC-1.

The greater abundance of relatively old (>300 Ka) calcite veins in VC-1 is consistent with the complex history of the area, where several hydrothermal events have occurred within the past 1 Ma [Wronkiewicz et al., 1984; Goff et al., 1986], and where volcanic activity has been continuing for the past 16.5

Ma [Gardner et al., 1986]. Abundant calcite veins have been observed in VC-2A drill core, obtained during drilling into the ~~vapor-dominated zone~~ post-caldera age hydrothermal system at Sulphur Springs during September, 1986 (F. Goff, personal communication, 1986). U-series age determinations of these veins may help constrain the chronology of ~~descent of the water table~~ evolution of the present hydrothermal system within Valles caldera.

You haven't said enough in the paper to justify the word 'descent'

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REFERENCES

Gardner, J.N., F. Goff, S. Garcia, and R.C. Hagan, Stratigraphic relations and lithologic variations in the Jemez volcanic field, New Mexico, J. Geophys. Res., 91, 1986.

Goff, F., J. Rowley, J.N. Gardner, W. Hawkins, S. Goff, R. Charles, D. Wachs, L Maassen, and G. Heiken, Initial results from VC-1, first Continental Scientific Drilling Program hole in Valles Caldera, New Mexico, J. Geophys. Res., 91, 1742-1752, 1986.

Goff, F. and L. Shevenell, Travertine deposits of Soda Dam, New Mexico and their implications for the age and evolution of the Valles Caldera hydrothermal system, Geol. Soc. Amer. Bull., (in press), 1987.

Ivanovich, M. and R.S. Harmon (eds.), Uranium Series Disequilibrium: Applications to Environmental Problems, 571 pp., Oxford University Press, Oxford, 1982.

Wronkiewicz, D., D. Norman, G. Parkison, and K. Emanuel, Geology of the Cochiti mining district, Sandoval County, New Mexico, Field Conf. Guideb., N.M. Geol. Soc., 35, 219-222, 1984.

Goff, F., ~~Shoven~~ L. Shevenell, J.N. Gardner, and C.O. Grigsby, The thermal regime of corehole VC-1 and the hydrothermal outflow plume of Valles Caldera, New Mexico, ~~this~~ JGR this volume

Vuataz, F.D., F. Goff, ~~Strontium isotopes of~~ ~~thermal~~ ~~waters and rocks~~ C. Fouillac, and J. Calvez, Strontium isotopes of thermal waters and rocks in the VC-1 corehole and the ~~Jemez Mount~~ Valles caldera region, Jemez Mountains, New Mexico, JGR this volume

Table 1. Description of Calcite Veins

Piece #	Depth (m)	Description*
225-9	449.6	coarse spar, clr, 4-8 mm
225-12A	450.8	coarse spar, clr-trl, vuggy, up to core width
228-11A	460.2	coarse spar, clr-trl, vuggy, 5-10 mm
229-12B	463.3	f-gr, wht-trl, growth-banded, 5-25 mm
251-5	515.1	coarse spar, clr, vuggy, 5-25 mm
319-5	723.6	f-gr, wht, sugary, 3-6 mm
326-5B	747.1	f-gr, wht, sugary, 3-6 mm
327-16A	749.5	f-gr, wht, sugary, 1-6 mm
343-17	794.7	f-gr, wht-trl, 2-7 mm
344-5	795.5	f-gr, complex w/sulf & phyl, banded, 15-20 mm
346-10	800.7	f-gr, complex w/sulf & phyl, banded, 12-14 mm
347-6	803.1	f-gr, pinkish-wht, 3-8 mm

*Most veins are near vertical except 344-5 and 346-10 have 40° dip. Abbreviations: clr=clear, trl=translucent, wht=white, f-g=fine-grained, sulf=sulfides, and phyl=phyllosilicates.

Table 2. U and Th Concentrations and Activity Ratios in Calcite Veins

Sample	U, ppm	Th, ppm	($^{235}U/^{238}U$)	($^{230}Th/^{232}Th$)	($^{230}Th/^{234}U$)	age, Ka*
225-9	0.100	0.041	1.15 (.09)	8.6 (1.9)	1.0000(.095)	>300
225-12A	0.034	0.039	1.10 (.05)	2.61(0.15)	0.892 (.056)	*223(+56,-37)
228-11A	0.02	0.02	--	--	--	--
229-12B	0.315	<0.01	1.05 (.07)	> 1000	1.067 (.093)	>300
251-5	0.041	0.040	3.41 (.37)	6.8 (1.6)	0.640 (.065)	*95±14
319-5	0.068	0.014	1.04 (.07)	14.4 (2.9)	0.973 (.082)	>300
319-6	0.122	0.034	0.96 (.08)	9.0 (1.6)	0.859 (.078)	*220(+105,-52)
326-5B	0.02	0.07	--	--	--	--
327-16A	<0.004	<0.03	--	--	--	--
343-17	0.01	0.08	--	--	--	--
344-5	0.649	0.028	1.01 (.04)	74 (35)	1.040 (.077)	>300
346-10	0.196	0.075	0.98 (.11)	9.3 (.26)	0.977 (.122)	>300
347-6	0.02	0.25	--	--	--	--

*See text for discussion of ages. Calculated initial ($^{234}U/^{238}U$) values are: 225-12A - 1.18±0.09; 251-5 - 4.16±0.49; and 319-6 - 0.93±0.14.